THE USE OF THERMOGRAVIMETRIC ANALYSIS TO FOLLOW THE CONVERSION OF COAL DERIVED RESIDS IN THE RESID RECYCLING PROCESS

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INTRODUCTION

Direct Coal Liquefaction produces a substantial amount of high boiling non-distillable product (resid). The amount and character of this material depends upon the coal used and the conditions and reaction times in the liquefaction process. Because of its high boiling point and potential thermal instability, this material is not suitable for processing in a conventional petroleum refinery. In a commercial liquefaction process as it is visualized today, therefore, this material would be recycled to the process. Indeed, it has also been shown to actually have a beneficial effect in the liquefaction process(1).

Since these resids are complex and high boiling materials, their performance in the recycling process is not well understood or currently predictable. To this end, considerable analytical work has been accomplished for characterization purposes(2-5). These analyses have not really provided information about the reactivity of these resids under recycle conditions. Some measure of the ability to convert these resids to lower boiling, fuel-grade products is critically needed for design and scale up purposes. For example, it is important to know whether all resids are alike in their convertability, what conditions were optimum for their conversion, and what catalyst if any is needed for the conversion.

This has motivated the development of a coal-derived resid reactivity research program at the University of Delaware. A critical part of this program has been the development of a laboratory scale batch reactor(6) (Short Time Batch Reactor, STBR) capable of running liquefactions up to 450°C and 2500 psi at well defined reaction times from a few seconds to 30 minutes or longer. This reactor is simple in design and can be conveniently operated in the laboratory. In this STBR equipment, we have made a preliminary study of the actual conversion of coal liquefaction non-distillable resids to lower boiling, lower molecular weight material under conditions closely approximating the direct coal liquefaction process.

These resid conversion studies required a reasonably convenient means of determining the conversion of the resid from any particular experiment. For this purpose, we have relied heavily upon Thermogravimetric Analysis (TGA) augmented with Gas Chromatography and to a lesser extent GC/MS.

EXPERIMENTAL

Apparatus

The design and operation of the STBR reactor system were described at the 1993 national American Chemical Society meeting in Chicago (6).

The thermogravimetric analyzer (TGA) used is a Model 51 TGA (TA Instruments, New Castle Delaware). The gas chromatography was done on a Hewlett-Packard HP 5970 series II GC using a flame ionization detector. The gas chromatography/mass spectrometry was also performed on a Hewlett-Packard HP5970 series II using HP Series mass selective detector.

Materials Studied

The two coal derived 850 °F distillation resids were obtained from the Wilsonville Pilot Plant Runs 259 and 260, and prepared and composited by CONSOL Research. They are solids which were ground by CONSOL to about fourteen mesh. Ultimate analyses for these two resids are shown in Table 1.

The catalyst used was a presulfided Ni/Mo on alumina catalyst (Shell 324) (10.5 wt% Mo and 2.08 wt % Ni). The catalyst was presulfided in a distillate oil at the Wilsonville Plant. The oil was removed and the catalyst dried and ground under nitrogen by CONSOL.

Resid Conversion Reactions

All reactions were run as mixtures of tetralin (T, the donor solvent) and resid (R) over a range of T/R ratios and temperatures with and without catalyst.

Reaction Product Workup Procedure

The reaction product work up procedure is given in Figure 1. This resulted in the production of a liquid filtrate which consisted mainly of tetralin with dissolved resid and a solid filter cake which consisted of unconverted or partially converted resid. These two fractions were analyzed separately to determine the amount of resid that was converted.

TGA analysis on the liquid filtrate, which contained most of the tetralin, confirmed

that there was no mineral matter in the liquid sample (see Figure 2). This is critical, as our conversion measurements were based on comparison of the ash content of the converted product with that of the unreacted resid. As shown in Figure 2, the tetralin content of the liquid filtrate as well as the amount of higher boiling materials which were soluble in the liquid could be determined by TGA in nitrogen. The liquid filtrate was also analyzed by GC/MS and GC to determine the number of compounds dissolved in the tetralin from the resid conversion and to determine, if possible, their identities. However, much of the resid material which dissolved in the tetralin, even after the liquefaction reaction under the conditions used, was still too low in volatility to be detected with GC or GC/MS. The soluble material in the liquid consisted of some low boiling conversion products of the tetralin, some material in the original resid that was tetralin soluble, and also material formed by breakdown of the resid into tetralin soluble substances.

The tetralin soluble resid plus that solubilized in the liquefaction process was estimated by comparison of the ash content of the solid filter cake with that of the unreacted resid. The filtered solid resid was dried in a vacuum oven at 100 °C for 48 hr, then ground in a mortar and pestle and dried again to remove any residual tetralin. This is important, as change of the resid by the tetralin occurs during the TGA analysis itself (see Figure 3). A TGA run on the filtered solid resid is shown in Figure 4. TGA runs on the filtered solid resids give several characteristic parameters, such as VM (volatile matter), FC (fixed carbon), and Ash for an un-catalyzed sample(7). By running in nitrogen at a ramp of 10°C/min to 600 °C, the amount of volatile matter (VM) can be determined. Then, by introducing oxygen at 600°C, the loss in weight was observed. It is due to the oxidation of the combustible materials in the resid, so called "fixed carbon (FC)", leaving the residue as mineral matter or ash. Thereafter, it is run at a ramp of 100 °C/min to 900 °C in oxygen to determine any further oxidation of the ash residue at higher temperatures. As shown in Figure 4, there is no further loss in weight for un-catalyzed samples.

Determination of Catalyst Concentration

For a catalyzed sample, the 600 °C-oxidized residue includes the ash from the resid and partially oxidized catalyst. Since the mineral matter (ash) from the resid was used as a reference for determination of conversion, the amount of the residue must be corrected for the catalyst added. A TGA run on a solid resid with catalyzed sample is shown in Figure 5. For this catalyzed sample, VM determined by TGA consists of VM from resid and weight loss of the catalyst; FC determined by TGA represents FC from resid and the first stage of catalyst oxidation; Ash_1 determined by TGA contains ash from the resid and partially oxidized catalyst; and Ash_2 determined by TGA includes ash from the resid and ash from the catalyst. During the second oxidation period, i.e., the interval of the temperature ramped at 100 °C/min to 1000 °C in oxygen and kept at 1000 °C for 120 min, an additional loss in weight was obtained. It is due presumably to the oxidation of the sulfided catalyst to the oxides. This can be translated into catalyst concentration by comparison of the weight loss at 1000 °C with the weight losses obtained on catalyst alone and a calibration sample. A TGA run on the pure sulfided catalyst is demonstrated in Figure 6. Running in nitrogen at 10 °C/min to 600 °C, the first drop in weight loss was detected. As oxygen was added at 600 °C, the second drop in weight loss was obtained. This loss in weight is due to the partial oxidation of the catalyst, designated as the first stage of catalyst oxidation. When finally running in oxygen from 600 °C at 100 °C/min to 1000 °C and holding at 1000 °C for 120 min, the third drop in weight loss was observed. This loss in weight was due to the complete oxidation of the catalyst, designated as the second stage of catalyst oxidation, leaving the residue (so called "Ash_2") as the ash from the catalyst, i.e., metal oxides. As mentioned above, this third drop in weight loss is solely caused by the second stage of catalyst oxidation, because there is no such drop for the un-catalyzed resid sample alone (see Figure 4). Therefore, the amount of catalyst present in the resid-catalyst mixture is proportional to the third drop obtained by TGA, i.e.,

$$Catalyst\ (wt\%) = \alpha\,(Ash_1(wt\%) - Ash_2(wt\%)) \qquad (1)$$

where α is a scale constant which can be determined by a calibration sample, Ash_1 a 600 °C residue (wt%), and Ash_2 a 1000 °C residue (wt%). The amount of ash from the resid can be estimated by the mass balance of the ash in the resid and that from the catalyst. Since the ash from the catalyst ($Ash_{catalyst}$) and the ash from the resid (Ash_{resid}) are unchanged throughout the reactor runs, their ratio should be a constant, i.e.,

$$k = \frac{Ash_{catalyst}(wt\%)}{Ash_{resid}(wt\%)}. \qquad (2)$$

The constant k can be determined by running a calibration sample. For a catalyst-resid mixture, the final residue (Ash_2) by TGA includes ash from the resid and ash from the

catalyst. Therefore, we have another equation which can be used to solve simultaneously with Equation 2 for the amount of the ash from the resid:

$$Ash_{catalyst}(wt\%) + Ash_{resid}(wt\%) = Ash_{2}(wt\%) . \quad (3)$$

Determination of Resid Conversion

Significant proportions of the resids are soluble in tetralin at room temperature (48 to 55 % for resid 1 and 37 to 42 % for resid 2 , depending on the tetralin to resid ratio). During the liquefaction process, particularly in the presence of a catalyst, further solid resid becomes soluble in the tetralin. To the extent that this solubilization represents conversion of the resid, it can be estimated by comparing the amount of ash present in the solid filter cake (X) with that of the unreacted resid (X_0). The total amount of resid dissolved in the tetralin, D, can be calculated using the equation:

$$D\ (wt\%) = (1 - \frac{X_0}{X}) \times 100\ (wt\%) . \quad (4)$$

D of course is the sum of the soluble resid and the resid which has become solubilized in the conversion process. Conversion can be estimated by subtracting the soluble portion of the resid D at time zero, from the D at time t. Equation 4 is valid because no inorganic matter (ash) goes into the liquid (see Figure 2). When catalyst is used, the ash determined by TGA must be corrected for the ash from the catalyst added.

RESULTS AND DISCUSSION

The experimental error for determination of the TGA characteristic variables (VM, FC, and Ash) is less than $\pm 0.5\%$ of the measured values. A TGA run on a liquid filtrate shown in Figure 2 gives two fractions: a fraction boiling in the tetralin range and a higher-boiling tetralin soluble fraction. TGA measurements can not discriminate among the converted components whose boiling points are close to tetralin. Therefore, GC and GC/MS were used to detect them. Tests on both un-catalyzed and catalyzed samples by GC and GC/MS have shown that there is some (up to 0.5 wt% for un-catalyzed runs, and 2 wt% for catalyzed runs) of material in the liquid filtrate boiling close to tetralin, which is formed by breakdown of resid. This represents about 5% to 20% conversion of the resid which has been converted to low boiling material. These low boiling substances consist of more than 50 individual compounds detected by GC, each too low in concentration to be identified. The GC/MS used in this work is not sensitive enough to detect these many low boiling materials in the very low concentrations involved.

The percent resid dissolved in tetralin (D) was calculated using Equation 4. A portion of the resid is tetralin soluble even at room temperature. To visualize the source of the dissolution portion in the resids under various conditions, resid-normalized VM, FC and D are plotted with various conditions for Resid 1 in Figure 7. It is obvious that the majority of the dissolution portion (about 80 wt%) comes from the VM in the resid.

For un-catalyzed 30 min reactor runs of Resid 1, the percent resid dissolved in tetralin (D) increases only about 1 wt% at 412 °C, and only about 6 wt% at 435 °C for T/R = 3.0 samples. For un-catalyzed 30 min reactor runs of Resid 2, the percent resid dissolved in tetralin (D) increases about 2 wt% at 410 °C, and about 13 wt% at 434 °C for T/R = 3.0 samples, which shows about twice the reactivity as resid 1.

Evolution rate versus temperature (DTG vs. T curve) of these uncatalyzed liquid samples were determined on the liquid filtrate from the calibration sample (treated with tetralin at room temperature), and resid 1 reacted for 5 min at 434 °C, and for 30 min at 435 °C. The results as plotted in Figure 8 indicate a bimodal distribution in the evolution pattern. There is no observable change in the evolution pattern through the reactor runs under the experimental conditions we have used in this project, although the material went into solution. A similar evolution rate vs. temperature of the liquid samples for the resid 2 conversion at 435 °C is obtained. There is also no significant change in the molecular weight distribution (evolution temperature pattern) in the liquid filtrate.

Plots of the D vs. reaction times for resid 1 at different temperatures and at T:R:Cat. (Tetralin:Resid:Catalyst) = 3:1:1 are shown in Figure 9. For reaction temperature around 415 °C, the percent resid dissolved in tetralin (D) increases with reaction time up to about 10% for 30 min (ten times higher than the un-catalyzed run). For a reaction temperature around 434 °C, the percent resid dissolved in tetralin (D) increases with reaction time up to 20 min, then it levels off. In 20 min, it increases to about 17% (four times higher than un-catalyzed runs). Plots of the D vs. reaction times for resid 2 at different temperatures and at T:R:Cat. = 3:1:1 are similar to the plots in Figure 9. For a reaction temperature around 415 °C, the percent resid dissolved in tetralin (D) increases with reaction time up to about 31.6% for 30 min (fifteen times higher than un-catalyzed runs). For a reaction temperature around 440 °C, it increases with reaction time up to 10 min, then it levels off. In 10 min, it

increases to about 33.2% (eight times higher than un-catalyzed runs). It is interesting to point out that:

1. in the lower temperature runs, they approached the same value of D in high temperature runs at longer reaction time (Figure 9);
2. at reaction time 30 min, the percent resid dissolved in tetralin (D) on an ash-free basis for 421 °C approaches about 87% and that for 442 °C to about 91%;
3. the reactivity of the resid 2 in catalyzed conversion is higher than that of the resid 1, the similar order which is observed in un-catalyzed conversion.

To examine the evolution pattern (a function of the molecular weight distribution) of the converted materials in the liquid filtrate, slow ramp TGA (1 °C/min) was run on selected liquid samples. Evolution rate vs. temperature of the liquid samples from the catalyzed resid 1 conversion: 0 min (the liquid filtrate from calibration sample, which is treated with tetralin at room temperature), 5 min at 434 °C, and 30 min at 435 °C for resid 1 was plotted in Figure 10. This shows that the evolution rate for reactor runs significantly shifted to lower temperature. In other words, there is a notable reduction in the average molecular weight by the catalyst. This can be quantitatively described by two characteristic variables: peak evolution temperature (T_{peak}) and mean evolution temperature (T_{mean}). T_{peak} is defined as the evolution temperature at maximum evolution rate. T_{mean} is defined as the mean evolution temperature weighted by the evolution rate. Mathematically,

$$T_{mean} = \frac{\sum_i (Evolution\ Rate)_i T_i}{\sum_i (Evolution\ Rate)_i}. \qquad (5)$$

The calculated T_{peak} and T_{mean} for the catalyzed runs and reference sample (at 0 min) are listed in Table 2. For longer reaction time, not only T_{mean} decreases by about 60 °C, but also T_{peak} shifted to lower temperature direction by about 50 °C. The same behavior was observed in the resid 2 catalyzed conversion. It is interesting to note from Figures 8 and 10 that the soluble fraction of the resids shows a bimodal distribution of differential evolution peaks in the TGA. The higher temperature peak disappears after catalytic reactions, but is unchanged in reactions without catalyst.

SUMMARY AND CONCLUSIONS

1. The combination of reaction in the STBR (Short Time Batch Reactor) with TGA analysis of the liquid filtrates and the "un-converted" filtered solid resids provides a direct and reproducible means of indicating the breakdown of coal-derived liquefaction resids under liquefaction conditions.
2. The conversion of resid to tetralin soluble material is determined by relating the inorganic matter (ash) in the reacted resid with that of the un-reacted resid. Conversion of un-catalyzed tetralin-insoluble resids to tetralin soluble products in this study was very low (< 10 wt%) under coal liquefaction conditions, however, up to 50 wt% of the resid is tetralin-soluble at room temperature.
3. Up to 80% (ash-free basis) of the room temperature tetralin insoluble resid is solubilized in tetralin using sulfided Ni/Mo on alumina catalyst at 434 °C for 10 min.
4. A method has been devised for determining the catalyst concentration and the ash from the resid by TGA.
5. The two resids examined showed somewhat different reactivities.
6. In the catalyzed experiments, a progressive decrease in the temperature evolution range (as measured by TGA) of the solubilized materials with time under liquefaction conditions is observed by TGA. In the un-catalyzed experiments, no change in the evolution range of the solubilized materials with time up to 30 min is observed by TGA.
7. The majority of tetralin soluble or solubilized materials come from the volatile matter in the resids.
8. While liquefaction conditions, particularly in the presence of Ni/Mo on alumina catalyst are effective in converting tetralin insoluble to tetralin soluble material and in reducing the average molecular weight (as shown by TGA), only a small fraction (perhaps 20 percent) of this material is converted to the boiling range of gasoline or diesel fuel under the liquefactions conditions studied (30 minutes at 434°C) as shown by GC.

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Table 1 Ultimate Analyses of the Two Resids

Sample	Ultimate (wt% MAF):	
Resid 1	C	90.24
Plant: Wilsonville	H	6.39
Run Number: 259	N	1.05
Sample Designator: V1067	S	1.49
Sampling Point: 2nd Stage Product	O (dif)	0.83
Feed Coal: Pittsburgh Seam, Ireland Mine	Ash, wt% as det.	10.21
Resid 2	C	91.03
Plant: Wilsonville	H	6.56
Run Number: 260	N	1.15
Sample Designator: V1067	S	0.09
Sampling Point: 2nd Stage Product	O (dif)	1.17
Feed Coal: Wyodak & Anderson Seam, Black Thunder Mine	Ash, wt% as det.	18.30

Table 2 Peak Evolution Temperatures (T_{peak}) and Mean Evolution Temperatures (T_{mean}) of the Liquid Filtrates from the Catalyzed Resid Conversion

Sample	T_{peak}, °C	T_{mean}, °C
Resid 1 + Catalyst		
0 min	320	349
5 min at 434 °C	318	322
30 min at 435 °C	273	291
Resid 2 + Catalyst		
0 min	307	321
30 min at 442 °C	274	282

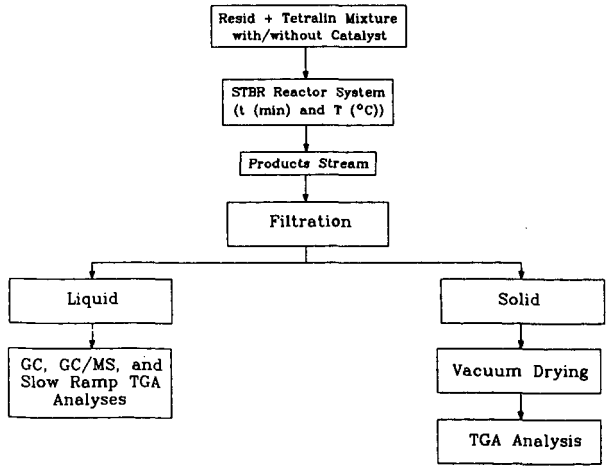

Figure 1 Schematic Diagram of the Experimental Procedure

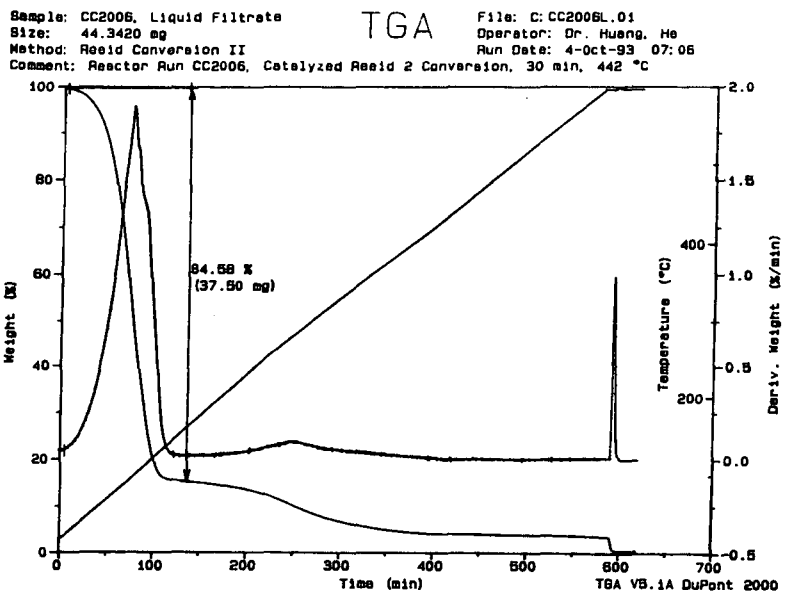

Figure 2 A TGA Run on a Liquid Filtrate of Catalyzed Reactor Run

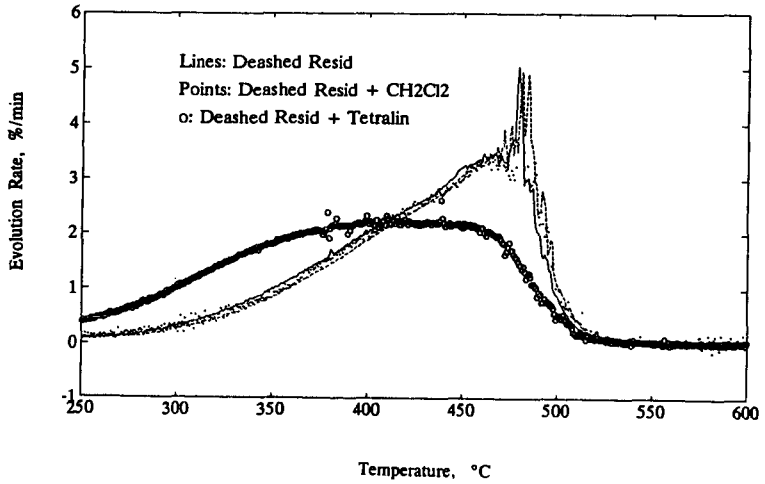

Figure 3 Effect of tetralin on TGA Analysis

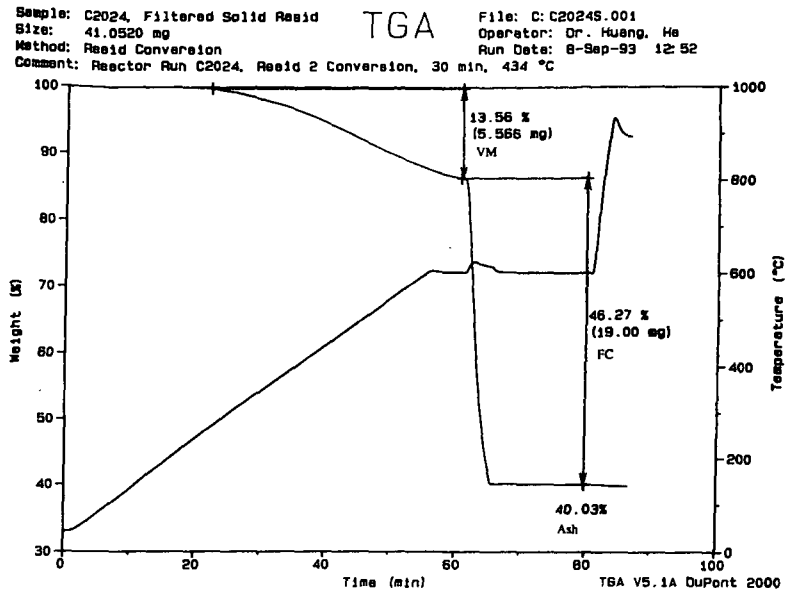

Figure 4 A TGA Run on a Filtered Solid Resid of Un-catalyzed Reactor Run

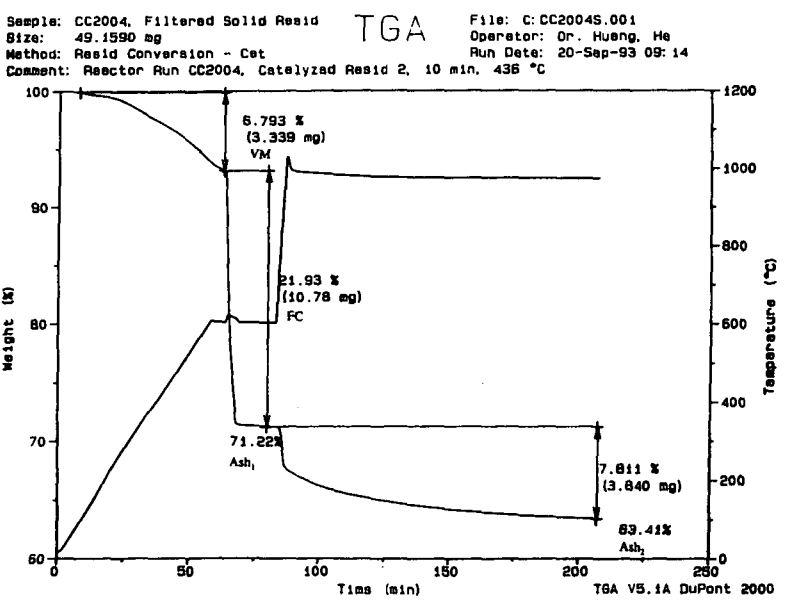

Figure 5 A TGA Run on a Filtered Solid Resid of Catalyzed Reactor Run

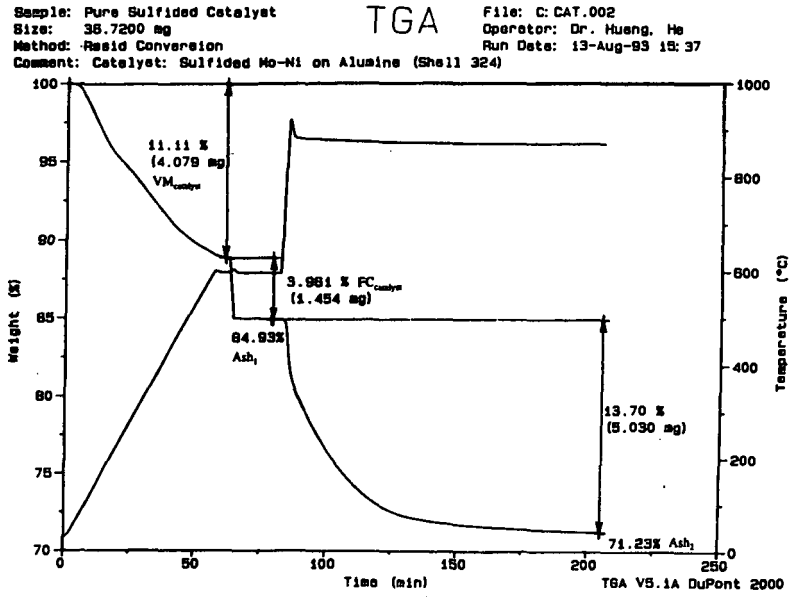

Figure 6 TGA Curves of the Pure Sulfided Catalyst of Mo-Ni on Alumina

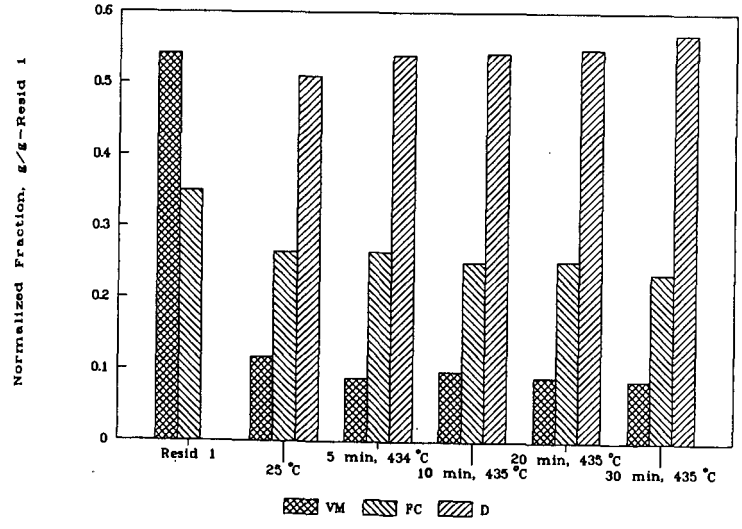

Figure 7 Resid-normalized VM, FC and D in the Resid 1 Treated or Reacted with Tetralin under Various Conditions (T/R = 3.0)

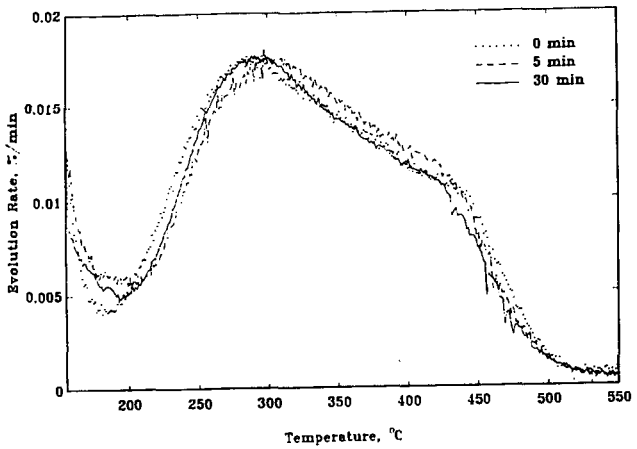

Figure 8 Evolution Rate (DTG) Versus Temperature Determined by Slow Ramp TGA (5 °C/min) for the Liquid Filtrates of Un-catalyzed Resid 1 Conversion (T/R = 3.0): 0 min, 5 min at 434 °C, and 30 min at 435 °C

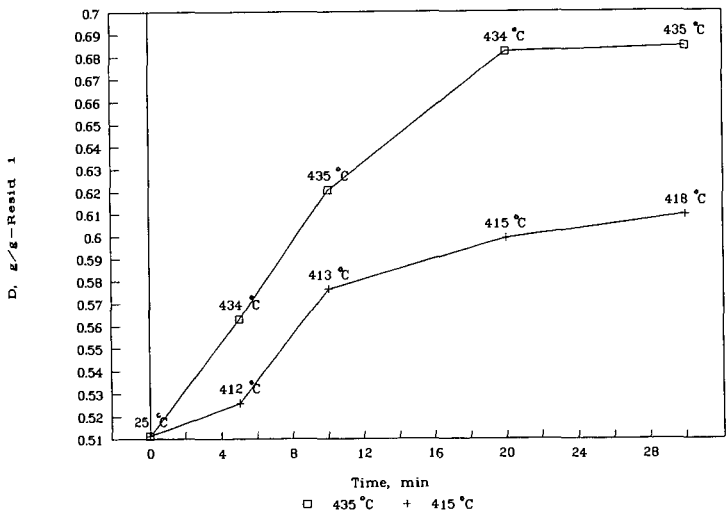

Figure 9 Percent Resid Dissolved in Tetralin (D) Versus Reaction Time of Catalyzed Resid 1 Conversion at Two Temperatures (T:R:Catalyst = 3:1:1)

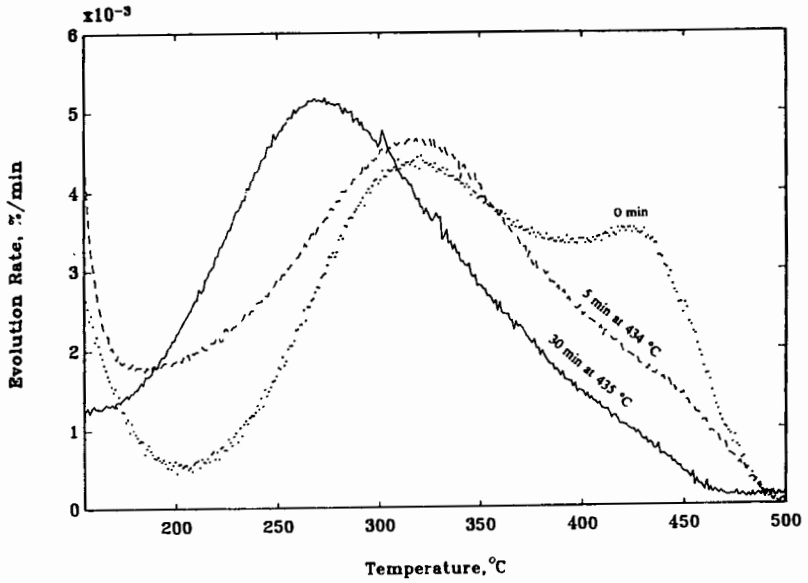

Figure 10 Evolution Rate (DTG) Versus Temperature Determined by Slow Ramp TGA (1 °C/min) for the Liquid Filtrates of Catalyzed Resid 1 Conversion (T/R = 3.0): 0 min, 5 min at 434 °C, and 30 min at 435 °C